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(54) Title: Process for Polymerization of Vinyl Chloride in Aqueous Emulsion

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For industrial emulsion polymerization of vinyl chloride radical-forming water-soluble catalysts, preferably salts of peroxysulfuric acid or hydrogen superoxide are used. To produce polyvinylchloride with industrially interesting properties the polymerization is conducted in the temperature range from 30 to 70°C. Especially in the case of low temperatures the polymerization rate increases initially only very slowly after the usual inhibition period so that the cooling capacity of the autoclave in the first phase is far from fully utilized. An adequate increase in the polymerization rate during the initial phase by increasing the concentration of the catalyst is impossible, because the reaction would otherwise be too violent in the later course so that the desired polymerization temperature can no longer be maintained. In this case the pressure in the autoclave also increases strongly, and in order to avoid dangerous situa-

tions the polymerization must be terminated by blowing the monomer off.

To avoid these disadvantages it has been proposed that the emulsion polymerization of vinyl chloride be conducted by using redox catalysts. In this case predominantly combinations of water-soluble peroxides such as hydrogen superoxide, persulfates and organic hydroperoxides with water-soluble reducing agents such as sulfite, thiosulfates, dithionites, and rongalites are used as redox systems. In many cases small quantities of salts such as iron, copper, manganese, chromium, cobalt, cerium, silver etc. salts are added as electron transfer agents.

In this operating procedure both the peroxide and the entire reducing agent are added to the batch at the beginning. As a result a sudden start in polymerization occurs but the reaction slows down increasingly as it progresses. In addition, in many cases the initial reaction is so violent that the generated heat of polymerization can no longer be totally dissipated, which can lead to undesirable and dangerous increases in the polymerization temperature. In practice no uniform polymerization process can be achieved with this method which, however, is of great importance for the economical production of polyvinylchloride and for the quality of the product. There is also an excessive consumption of peroxide, because part of the peroxide is consumed by a secondary reaction with the reducing agent without forming radicals.

In order to avoid the slowing down of the reaction after the violent polymerization start, in another process partial quanti-

ties of the peroxide and of the reducing agent are metered in. This operating procedure also leads to a nonuniform and scarcely controllable polymerization process, and it is impossible to utilize the entire cooling capacity of the autoclave during the entire polymerization time. Rather in order to assure operational safety, over a broad range of polymerization it is necessary to conduct it considerably below the maximal utilization since otherwise, because of the uncontrollable fluctuations, the accumulating heat of polymerization may possibly exceed the cooling capacity, and an interruption of the polymerization process by blowing off the monomers will become inevitable.

A process for polymerization of vinyl chloride or mixed polymerization of vinyl chloride and ethylenically unsaturated monomers, up to 40 wt.% relative to the copolymerizate, in aqueous emulsion by using a redox catalyst system consisting of a water-soluble reducing agent, water-soluble peroxides and copper or iron salts in the presence of emulsifiers and possibly buffering substances has been devised. The process is characterized by the fact that one works at temperatures from -20 to 80°C under a pressure of 1 to 200 atg¹, the entire reducing agent is added at the beginning in quantities of 0.005-1 wt.%, preferably 0.01 to 0.5 wt.% relative to the monomer to the polymerization batch and the entire quantity of peroxide is metered in continuously.

It is surprising that the rate of polymerization can be precisely controlled by the process according to the invention. It has also been found to be especially advantageous to meter of

¹atg=atmospheres, gauge

the peroxide in continuously in such a way that the cooling capacity of the reaction vessel is fully utilized during the entire polymerization time. There is no danger to operational safety, because in the polymerization batch as much peroxide is always present as is precisely needed in order to maintain the polymerization rate. The metering rate is reduced upon even a slight increase in temperature. This causes an immediate reduction in the rate of polymerization so that the preselected reaction temperature is restored.

Another advantage of the process is that upon the interruption of the metering the polymerization comes to a stop in a few minutes. In emergency cases therefore no blow-off of the monomer is required; rather it is sufficient to adjust the metering. Through this possibility of precisely controlling the polymerization rate it becomes possible to operate with a fully utilized cooling capacity without having to fear a violent course of the polymerization. From this a considerable saving in time results per polymerization batch and therefore greater economy of the process according to the invention.

In addition considerably less peroxide, e.g., only one fifth as much, is consumed, because due to the redox reaction during the metering in of the peroxide an optimal utilization of the peroxide is achieved. The peroxide is added for the most part by a continuously regulated metering pump. This may be operated manually or advantageously controlled automatically.

The metering depends on the exit temperature of the cooling water. In such cases it is especially favorable to conduct

continuous metering in such a way that the temperature of the reaction mixture (and with it also the pressure in the autoclave) and the exit temperature of the cooling water are constant. The best utilization of the reaction vessel is achieved when the exit temperature of the cooling water always has the value which is just enough to keep the temperature of the reaction mixture from rising. In the case of automatic control of the metering pump upon a slight increase in temperature above the nominal value the metering rate is automatically reduced, and if the temperature drops slightly, the metering rate is automatically increased. The manual control is accomplished in the same manner in which case the operator is informed by the temperature or pressure registration gauge of the polymerization conditions.

As reaction vessels for the most part water-cooled autoclaves are used which are frequently equipped with agitators and baffle plates. In addition the autoclaves may also be equipped with reflux condensers in order to increase their cooling capacity. The polymerization may be conducted in batches, frequently with secondary metering in of the monomer, or continuously, e.g., by connecting several autoclaves in series according to the so-called cascade process. In such cases temperatures of -20 to 80°C , preferably 0 to 65°C and pressures of 1 - 200 atg are used. In the case of homopolymerization and in the case of mixed polymerization of comonomers which do not have a high vapor pressure, pressures of 1 - 20 , preferably 2 - 15 atg are sufficient. However, if olefins such as ethylene are copolymerized then pressures of 20 - 200 atg are necessary.

At low temperatures antifreezing agents such as methanol, ethanol or glycols are added to the aqueous phase. Polymerization can also be conducted by charging a seed latex.

The catalyst redox system consists of water-soluble peroxides, water-soluble reducing agents and copper or iron salts as electron transfer agents.

As water-soluble peroxides advantageously salts of peroxy-sulfuric acids such as ammonium persulfate, potassium persulfate or sodium persulfate come into consideration. However, hydrogen superoxide, tert.butyl hydroperoxide or other water-soluble peroxides and mixtures of various water-soluble peroxides may be used. The peroxides are metered in according to demand but usually dissolved in water. In such cases it has been found that for almost all types of polymerization three typical phases occur during the metering. Initially and briefly a strong rapidly diminishing consumption appears which is followed by a long phase of slowly diminishing consumption. Toward the end of the polymerization a distinct increase in the quantity to be metered in occurs briefly once more.

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For the process according to the invention reducing agents such as thiosulfates, rongalite, dithionites, sulfites and their mixtures are suitable. Sulfites and rongalite are preferably used. The quantities employed in such cases are between 0.01-0.1 wt.% relative to the monomer.

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The third component of the redox system consists of copper or iron salts. In this case quantities of 0.05-10 ppm are used relative to the metal/monomer.

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As the copper salts both copper I salts such as copper I halides, as well as copper II salts such as copper II halides, copper sulfate, and copper nitrate come into consideration. Also poorly soluble copper II salts such as the phosphate, sulfide, ferrocyanide, and arsenite are of importance especially if fat soaps such as alkali or ammonium salts of lauric acid, myristic acid, palmitic acid, stearic acid or synthetically branched carboxylic acids such as Versatic acid (registered trademark of the Shell Company) or isotricedanic [*sic*, ?*isotridecanoic*] acid (Ruhrchemie) are used as emulsifiers. The poorly soluble salts may be added both as such and also synthesized "in situ" in the reaction vessel. The copper salts are preferably added in quantities of 0.1-1 ppm relative to the copper/monomer. In addition copper may also be used in metallic form. In this case the copper is oxidized in the reaction mixture by the peroxide into copper I or copper II. The iron salts may be used both in divalent and trivalent oxidation stages. For example, halides, sulfates, nitrates may be used, preferably in quantities of 1-10 ppm relative to the iron/monomer. — *Hughes*

Metallic iron may also be used. It is also possible to use mixtures of copper and iron salts or metals.

The emulsifiers required for emulsifying the monomers are added in quantities of 0.5 to 3 wt.% relative to the monomer. In this case the commonly used anionic emulsifiers such as fatty soaps, alkyl sulfates, alkane sulfonates, alkylbenzene sulfonates, alkyl naphthalene sulfonates, sulfosuccinic acid esters, partial phosphoric acid esters or cationic emulsifiers such as

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alkylammonium salts or amphoteric emulsifiers, e.g., partial fatty acid esters of polyvalent alcohols such as sorbitol monopalmitate, fatty alcohol sulfuric acid esters, partially etherified polyalcohols, condensation products of alkaline oxides with higher fatty acids or higher fatty alcohols or phenols as well as their mixtures may be added. The emulsifiers may either be charged all at once or metered in in portions. It is also possible to synthesize some emulsifiers "in situ" and in this case, for example, to charge one component all at once and meter the other in. Mixtures of emulsifiers or additional suspension agents may also be used.

As buffers all substances described for emulsion polymerization of vinyl chloride may be added such as sodium carbonate, sodium bicarbonate, alkali acetates, borax, alkali phosphates. Ammonia or ammonium salts of carboxylic acids are also applicable, especially together with iron salts or with copper ferrocyanide or ferricyanide.

If necessary, regulators such as aliphatic aldehydes with 2-4 carbon atoms, chlorinated hydrocarbons such as dichloro- and trichloroethylene, chloroform, methylene chloride, mercaptans, propane and isobutylene may be jointly used.

The process according to the invention is not limited to the homopolymerization of vinyl chloride but rather other ethylenically unsaturated monomers may be mixed-polymerized. As comonomers in particular one can mention the vinyl halides such as vinyl fluoride, vinylidene fluoride, vinylidene chloride, vinyl esters of straight chained or branched carboxylic acids with 2-

20, preferably 2-4 carbon atoms such as vinyl acetate, vinyl propionate, vinyl butyrate, vinyl-2-ethylhexoate, vinyl versatate (Versatic acid is a registered trademark of Shell Company for carboxylic acid mixtures available on the market), vinyl isotridecanoic acid esters, vinyl ethers, unsaturated acids such as maleic, fumaric, itaconic, crotonic, acrylic, methacrylic acid and their monoesters or diesters with monoalcohols or dialcohols with 1-10 carbon atoms; also olefins such as ethylene, propylene, isobutylene, styrene and acrylonitrile may be mentioned.

The emulsions are usually produced with a solids content of up to 50 wt.%. They are processed by known methods by spray drying, roller drying, or coagulation.

The polyvinylchloride thus produced contains no excessive peroxide as a result of metering in the peroxide according to the invention and is therefore characterized by an outstanding heat and light stability.

Example 1 (reference)

A 2 cbm stirring autoclave is charged with:

950 kg	water
56 kg	seed latex (emulsion with 40 wt.% polyvinyl chloride)
0.15 kg	dodecylbenzene sulfonate
280 g	sodium bicarbonate
800 g	potassium persulfate

After 15 minutes of evacuation to 20 Torr 120 kg of vinyl chloride are introduced and the contents of the reactor is heated to 43°C and polymerized while stirring at 60 rpm at that temperature. When the pressure drops by 0.5-1 atg, 100 kg of vinyl chloride and 7 kg of a 10% dodecylbenzene sulfonate solution are pumped in 7 times in each case. After the last metering, upon a

pressure drop of 3 atg the remaining monomer is distilled off.
The vinyl chloride metering is performed after the following times:

7^h, 13^h, 18^h, 23^h, 27^h, 33^h, 38^h.

The total running time up to a pressure of 3 atg (90% conversion) was 53 hours. An emulsion with about 42 wt.% solids content was obtained.

Example 2 (reference)

A batch such as that in Example 1 but with the addition of 2 g of copper sulfate with 5 waters of crystallization and with 120 g of sodium sulfite in aqueous solution metered in upon the reaching of the polymerization temperature of 43°C had the following course of the individual vinyl chloride doses:

3^h, 5^h, 8^h, 11^h, 15^h, 20^h, 28^h.

The total running time up to a pressure of 3 atg was 36^h. The decrease in the reaction rate in the course of the polymerization is typical.

Example 3 (reference)

A batch such as that in Example 1 but with the addition of 2 g of copper sulfate with 5 waters of crystallization and with 160 g of sodium sulfite metered in upon the reaching of the polymerization temperature of 43°C had the following course of the vinyl chloride metering:

2^h, 3^h, 4^h, 5½^h, 7^h, 10^h, 14^h.

The total running time was 20 hours (up to a pressure of 3 atg).

Example 4 (reference)

A batch such as that in Example 1 but with the addition of 2 g of copper sulfate with 5 waters of crystallization and with 200 g of sodium sulfite metered in upon reaching the polymerization temperature of 43°C was given the first dose of monomer after 1 hour and then displayed a violent reaction so that the temperature could no longer be maintained and after another half hour the polymerization had to be interrupted by depressurizing the monomer.

Example 5

A 2 cbm stirring autoclave was charged with:

950 kg	water
56 kg	seed latex (40 wt.% solids content of polyvinyl chloride)
0.15 kg	Dodecyl benzene sulfonate
280 g	Sodium bicarbonate
2 g	Copper sulfate with 5 waters of crystallization
250 g	Sodium sulfite

After 15 minutes of evacuation to 20 Torr, 120 kg of vinyl chloride was pumped in, the reactor contents heated to 43°C and the metering of a 2% potassium persulfate solution was begun. The persulfate solution was metered in at such a speed that a rapid and uniform polymerization was achieved. The 7 doses of vinyl chloride of 100 kg each were added in time intervals from 45-50 minutes. The total running time up to 3 atg was about 7 hours. The persulfate consumption was

<u>Hour</u>	<u>1st</u>	<u>2nd</u>	<u>3rd</u>	<u>4th</u>	<u>5th</u>	<u>6th</u>	<u>7th</u>
g	45	35	18	14	12	8	14

for a total of 146 g. An emulsion with 43 wt.% solid content was formed.

In a repeated batch the rate of a persulfate metering was increased until the polymerization heat could no longer be carried off and the temperature and pressure reaction was brought under control again after only 2 minutes.

Example 6

A batch such as in Example 5 but with 20 g of iron II chloride instead of copper sulfate lasted a total of 10 hours and consumed 250 [g] of potassium persulfate. The metering was continued in such a way that the temperature of the reaction mixture and that of the exit temperature of the cooling water was constant over the entire polymerization time.

Example 7

A batch such as in Example 5 but using 200 g of rongalite instead of sodium sulfite and 1.5 g copper II chloride instead of copper sulfate could be conducted in the same manner with the same metering rates.

Example 8

A 2 cbm autoclave was charged with:

950 kg	water
8 kg	Texapon K 12 (trademark of the Henkel Company)
270 g	Sodium bicarbonate
2 g	Copper sulfate with 5 waters of crystallization
500 g	Sodium sulfite

After the evacuation to 20 Torr 800 kg of vinyl chloride were pumped in and 40 kg of propylene were pressed in. At a reactor temperature of 43°C the metering of the ammonium persulfate was begun. The polymerization lasted a total of 11 hours (at 5 atg it was terminated) and 300 g of persulfate were consumed. The persulfate was metered in continuously in such a way

that the exit temperature of the cooling water always had the value which was just sufficient to keep the temperature of the reaction mixture from rising above 43°C.

Example 9

A 2 cbm stirring autoclave was charged with:

950 kg	water
8 kg	Lauric acid
200 g	Sodium hydroxide
2 g	Copper sulfate with 5 waters of crystallization
3 g	Potassium ferrocyanide with 3 waters of crystallization
250 g	Sodium sulfite

After evacuation to 20 Torr 120 kg of vinyl chloride were pumped in, the reactor contents heated to 50°C and the metering of a 2% potassium persulfate solution was begun. When the pressure dropped 100 kg of vinyl chloride and 2 kg of 10% caustic soda were pumped in 7 times.

The rate of the persulfate metering was controlled in such a way that a maximal utilization of cooling capacity was always present. The metering of the vinyl chloride was performed at time intervals of 45 minutes in each case. The total running time was 6 hours. The persulfate consumption was 120 g.

Example 10

A batch according to Example 9 but using the equivalent quantity of ammonia instead of sodium hydroxide could be polymerized in the same manner.

Example 11

A 2 cbm stirring autoclave with charged with:

950 kg	water
2 kg	Texapon K 12 (trademark of the Henkel Company)
1 kg	Sodium acetate
2 g	Copper sulfate with 5 waters of crystallization

250 g Sodium sulfite

After evacuation of the autoclave 20 kg of vinyl acetate and 100 kg of vinyl chloride were pumped in and the reactor heated to 54°C. At this temperature the metering of a 2% potassium persulfate solution was begun. The persulfate solution was metered according to the polymerization curve.

During the polymerization 80 kg of vinyl acetate, 700 kg of vinyl chloride and 60 kg of a 10% Texapon solution were metered in continuously within 5 hours.

The polymerization was completed after 7 hours. The persulfate consumption was 100 g.

Example 12

A batch according to Example 11 with vinyl laurate instead of vinyl acetate lasted 10 hours. Within 8 hours the vinyl laurate and the vinyl chloride were metered in. The potassium persulfate consumption was 140 g.

Example 13 (reference)

A 25 cbm stirring autoclave equipped with a reflux condenser and with a cooling area of 36 m² was charged with:

- 10,600 kg water
- 600 kg Seed latex (42% solids content on polyvinyl chloride)
- 7 kg Sodium bicarbonate
- 17 kg Potassium persulfate

After evacuation of the reactor 6,500 kg of vinyl chloride were pumped in, the batch was heated to 43°C and polymerization conducted with stirring at this temperature. 2 hours after the polymerization temperature was reached 3,500 kg of vinyl chloride and 420 kg of 10% dodecylbenzene sulfonate were metered in

continuously within 15 hours. The total running time was 24 hours at a cooling water inlet temperature of 14°C.

Example 14

A 25 cbm stirring autoclave equipped with a reflux condenser and with a cooling area of 36 m² was charged with:

10,600	kg	water
600	kg	Seed latex (42% solids content on polyvinyl chloride)
7	kg	Sodium bicarbonate
2.5	kg	Rongalite

After evacuation of the reactor 6,500 kg of vinyl chloride were pumped in and the batch was heated to 43°C. At this temperature the metering of a 2% potassium persulfate solution was begun. The metering rate was regulated automatically as a function of the exit temperature of the cooling water in such a way that cooling effect was just sufficient to keep the temperature of the batch at 43°C. During the polymerization 3,500 kg of vinyl chloride and 420 kg of 10% dodecylbenzene sulfonate solution were metered in continuously within 6 hours. The total running time of the batch was 9 hours. The persulfate consumption was 3.5 kg.

Example 15

A 16 liter stirring autoclave of V2A steel was charged with:

4.0	kg	water
80	g	Dodecylbenzene sulfonate
60	g	Nonylphenol polyglycol ether (arcopal)
10	g	Sodium bicarbonate
10	mg	Copper sulfate with 5 waters of crystallization
10	g	Rongalite

When to remove the air it was evacuated to 20 Torr and 3.0 kg vinyl chloride and 3.0 kg of ethylene were pumped in.

By cooling with brine of -15° an internal temperature of $+10^{\circ}\text{C}$ was reached. AT that time a pressure of 40 atm was adjusted. Then the metering of the potassium persulfate was started. The metering was conducted in such a way that a maximal utilization of the cooling capacity was always present. The consumption of persulfate was 11 g. After a polymerization time of 10 hours polymerization was terminated and the excess ethylene blown off. A stable emulsion with a solids content of 48 wt.% was obtained. 3.6 kg of copolymerizate with 18 wt.% ethylene were obtained by coagulation (K value 78).

Claims

1. Process for polymerization of vinyl chloride or mixed polymerization of vinyl chloride and ethylenically unsaturated monomers up to 40 wt.% relative to the copolymerizate in aqueous emulsion by using a redox catalyst system consisting of water-soluble reducing agents, water-soluble peroxides and copper or iron salts in the presents of emulsifiers and possibly buffering substances characterized by the fact that by working at a temperature of -20 to 80°C , preferably 0 to 65°C at a pressure of 1-200 atg the entire reducing agent is added in quantities of 0.005-1 wt.%, preferably 0.01-0.5 wt.% relative to the monomer to the polymerization batch, and the entire peroxide quantity is metered in continuously.
2. Process as in claim 1 characterized by the fact that the poorly soluble copper salts are used in quantities from 0.05-10 ppm relative to the copper/monomer and fatty soaps as emulsifiers.

3. Process as in claims 1 and 2 characterized by the fact that the continuous metering of the peroxide is conducted in such a way that the cooling capacity of the reaction vessel is fully utilized.

4. Process as in claims 1 and 2 characterized by the fact that the continuous metering of the peroxide is conducted in such a way that the temperature of the reaction mixture and the exit temperature of the cooling water are held constant.

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